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## (54) REFRIGERATING MACHINE OIL COMPOSITION

(57)Abstract:

PURPOSE: To obtain a refrigerating machine oil composition, comprising a hydrofluoroalkane and a specific mixed ester, capable of ensuring a prescribed level or above of viscosity, having a high electrical resistance value, excellent in compatibility with a refrigerant and seizure resistance and suitable as a refrigerating machine oil, etc., for a refrigerator having a hermetically closed type compressor.

CONSTITUTION: This refrigerating machine oil composition comprises (A) a refrigerant composed of one or more hydrofluoroalkanes which are substitute refrigerants for a hydrofluorocarbon R134a (HFC-134a) or a hydrochlorofluorocarbon R22 (HFC-22) and (B) a mixed ester of a hydroxypivalic acid ester expressed by the formula [R and R' each is a linear part and a 2-10C alkyl; (n) is 1-5] with an aliphatic ester composed of a fatty acid and an aliphatic alcohol.



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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] About the refrigerating-machine-oil constituent which uses the refrigerant which consists of at least one sort of hydro fluoroalkane, its electric resistance value is high while this invention secures the viscosity more than fixed (VG68), and it relates to the refrigerating-machine-oil constituent excellent in especially compatibility with a refrigerant.

#### [0002]

[Description of the Prior Art] Although chlorine content refrigerants, such as R11 (CFC13), R12 (CF<sub>2</sub>Cl<sub>2</sub>), R123 (CF<sub>3</sub>CHCl<sub>2</sub>), and R22 (CHCl<sub>2</sub>F), are conventionally used as a refrigerant in the refrigerator, Development of a chlorofluorocarbon-replacing material makes it urgent from an environmental problem. Recently, R134a (CF<sub>3</sub>CH<sub>2</sub>F), and R32 (CH two F<sub>2</sub>), R125 (CHF<sub>2</sub>CF<sub>3</sub>), R290 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>), The hydro fluoroalkane system refrigerant of non-chlorine systems, such as R717 (NH<sub>3</sub>) and R143a (CF<sub>3</sub>CH<sub>3</sub>), is proposed, and these refrigerants and ester oil with compatibility are proposed as refrigerating machine oil. For example, JP,4-72390,A has the indication of the ester of the hindered polyols which have a specific radical. Moreover, although using pentaerythritol ester as refrigerating machine oil is put in practical use in the electric refrigerator, the viscosity in 40 degrees C is 32mm<sup>2</sup>/s. There is a problem that it cannot apply as refrigerating machine oil for freezers which uses direct-vent-system compressors, such as a large-sized air conditioner with which a low high viscous (the viscosity in 40 degrees C is 68mm<sup>2</sup>/s above) thing is demanded, rotary system, a scrolling type, and a screw type. Moreover, since a motor is in refrigerating machine oil, the freezer which has these direct-vent-system compressors requires the volume resistivity more than 2x10<sup>14</sup>-ohmcm (25 degrees C) still more preferably more than 5x10<sup>13</sup>-ohmcm (25 degrees C) preferably more than 1x10<sup>13</sup>-ohmcm (25 degrees C) as refrigerating machine oil.

[0003] this invention person etc. receives the refrigerant of R134a, R125, R143a, and R32 grade, Although it found out having printing-proof nature while hydroxy pivalate ester showed compatibility high in spite of hyperviscosity, hydroxy pivalate ester has structure gestalten, such as oligomer, cannot remove easily the esterification catalyst used on the occasion of that manufacture, and has a problem as refrigerating machine oil for this kind of direct-vent-system compressors, and high insulating ester oil is demanded.

#### [0004]

[Problem(s) to be Solved by the Invention] This invention is a refrigerating-machine-oil constituent which uses the refrigerant which consists of at least one sort of the hydro fluoroalkane which is the alternative refrigerant of R134 22 [ a ] chlorofluorocarbon, and offers a technical problem the refrigerating-machine-oil constituent which is excellent in insulation while securing the viscosity more than fixed level, and is excellent in especially compatibility with a refrigerant.

#### [0005]

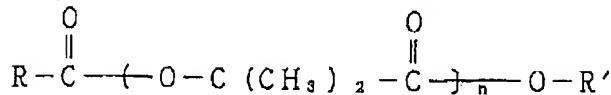
[Means for Solving the Problem] The refrigerating-machine-oil constituent of this invention is characterized by consisting of mixed ester with the aliphatic series ester which this refrigerating-

machine-oil constituent becomes from the hydroxy pivalate ester shown by the following general formula (1), and a fatty acid and fatty alcohol in the refrigerating-machine-oil constituent which uses the refrigerant which consists of at least one sort of hydro fluoroalkane.

[0006]

[Formula 2]

一般式 (1)



[0007] (The alkyl group of the shape of the straight chain with which the inside R of a formula and R' have 2-10 carbon atoms in a straight chain part, or branching, and n are the integers of 1-5)

Moreover, the refrigerating-machine-oil constituent of this invention is mixed ester with the aliphatic series ester which this refrigerating-machine-oil constituent becomes from the hydroxy pivalate ester shown by the above-mentioned general formula (1), and a fatty acid and fatty alcohol in the refrigerating-machine-oil constituent which uses the refrigerant which consists of at least one sort of hydro fluoroalkane, and the carbon number of an end alkyl group is characterized by ten or less carbon number and a solubility parameter being [ 8.8 or more and molecular weight ] 900 or less in a straight chain part.

[0008] The refrigerating-machine-oil constituent of this invention explains the target hydro fluoroalkane refrigerant. R32, R134a, R125, R290 (propane), as a hydro fluoroalkane refrigerant It is any one sort of R717 (ammonia) and the R143a, or its mixed refrigerant. for example, the case of the mixed refrigerant of R22 alternative -- R32/R125=60 / 40 (% of the weight --) Like the following R32/R134a=30/70, R32/R125/R134a=10/70/20, R32/R125/R134 a/R290=20/55/20/5, R32/R125/R134a=30/10/60, R125/R143a=45/55, R125/R143 a/R134a=40/45 / 15 grades are mentioned.

[0009] Next, the refrigerating-machine-oil constituent of this invention is explained. first, as aliphatic series ester which consists of the hydroxy pivalate ester and the fatty acid which are shown by the above-mentioned general formula (1), and fatty alcohol The solubility parameter (S.P. is said MJ/m<sup>3</sup> and the following) highly (8.8 or more [ Preferably ]) Moreover, it is desirable that the carbon number of an end alkyl group is ester with few (preferably carbon numbers 6-9) still lower (900 or less [ Preferably ]) weight average molecular weight in a straight chain part, and thereby, while excelling in compatibility with the above-mentioned refrigerant, printing-proof nature is also securable.

[0010] An "end alkyl group" is an alkyl group combined through oxy-carbonyl association in ester, and it does not have a functional group. Moreover, a solubility parameter is calculated by the approach of Fedors and indicated by Kodansha Issue on 1 excellent-book "practical use macromolecule for engineer" 73 page -77 page besides Junji Mukai, and October 1, 1981. moreover, the molecular weight of ester oil -- the case of a single compound -- the case of the formula weight and mixture -- the mixing ratio of the formula weight of each compound -- in the case of the value and oligomer which are measured by average, it is the weight average molecular weight.

[0011] Hereafter, it explains concretely. first, the alkyl group of the shape of the alkyl group of the shape of the straight chain with which R in the above-mentioned general formula (1) and R' have 2-10 carbon atoms in a straight chain part as hydroxy pivalate ester from a viewpoint of compatibility with an above-mentioned refrigerant, and printing-proof nature, or branching, the straight chain which has 3-9 carbon atoms in a straight chain part preferably, or branching -- they are an iso heptyl radical, an isobutyl radical, and an isopentyl radical still more preferably. moreover, n -- the integer of 1-5 -- it is -- desirable -- 1-3 -- it is 1-2 still more preferably.

[0012] Moreover, it may be esterified and obtained with the fatty alcohol which has the alkyl group of the shape of the straight chain which has 2-10 carbon atoms for the mixed acid of hydroxy pivalate and a dibasic acid in a straight chain part, or branching as hydroxy pivalate ester. Specifically, hydroxy pivalate ester [ of an iso heptyl radical ], R, and R' is mentioned [ the hydroxy pivalate ester of an

isopentyl radical etc. ] for R in the above-mentioned formula, and R'. The hydroxy pivalate ester obtained according to esterification contains esterification catalysts, such as an alkali-metal catalyst added in the manufacture process, and an electric resistance value is usually 1x10<sup>12</sup>-ohmcm - 1x10<sup>13</sup>-ohmcm (25 degrees C) extent.

[0013] Next, the ester mixed with this hydroxy pivalate ester is explained. The ester oil of polyol esters, multiple-valued carboxylate, fumaric-acid ester oligomer, carbonates, hydronium KISHIBI valine acid ester, and those combination is mentioned, and as for all, it is desirable that the solubility parameter is high (8.8 or more [ Preferably ]), and the carbon number of an end alkyl group is ester with few (preferably carbon numbers 6-9) still lower (900 or less [ Preferably ]) weight average molecular weight in a straight chain part, and, thereby, it can do with what is excellent in compatibility with the above-mentioned refrigerant.

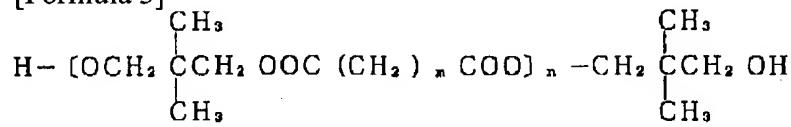
[0014] As polyol esters, polyol esters with the fatty acid of the shape of (1) aliphatic-series polyhydric alcohol, the shape of a straight chain, and branching Or partial ester with the fatty acid of the shape of the partial ester, the diester of (2) neopentyl glycol and a fatty acid, (3) aliphatic-series polyhydric alcohol, the shape of a straight chain, and branching The ester of the aliphatic series dibasic acid of the shape of complex ester with the aliphatic series dibasic acid of the shape of the shape of a straight chain, and branching, the shape of (4) straight chains, and branching, and fatty alcohol, (5) monovalence fatty alcohol, and those isomers, For example, ethyleneoxide, propylene oxide, butylene oxide, The alkylene oxide chosen from those isomers, such as amylene oxide, preferably one mol - ten mols Polyhydric alcohol, such as a 1-6-mol addition product, (6) glycerols, and trimethylol propane, Alkylene oxide preferably one mol - ten mols A 1-6-mol addition product, (7) The diester of the alkylene oxide addition product of monovalence fatty alcohol, and an aliphatic series dibasic acid (8) Ester with the fatty acid of the shape of the 1 - ten-mol addition product of the alkylene oxide of polyhydric alcohol, such as a glycerol and trimethylol propane, the shape of a straight chain, and branching is mentioned.

[0015] As the above-mentioned polyol esters, specifically The ester of pentaerythritol and a 2-ethylhexyl acid [molecular weight 640 and the S.P. value 9.1], ester (molecular weight 685 and S.P. value 8.9] --) with a mixed acid with pentaerythritol, a 2-ethylhexyl acid / 5, and a 5-trimethyl hexanoic acid [ 3 and 5 ] Ester of pentaerythritol and n-pentyl acid (molecular weight 472, S.P. value 9.6], mixed ester of pentaerythritol, and an n-pentyl acid / n-hexyl acid (ester, such as molecular weight 500 and S.P. value 9.5], is mentioned.) Moreover, ester of an adipic acid and isooctyl alcohol (ester of molecular weight 342, S.P. value 8.9], a succinic acid, and isooctyl alcohol (molecular weight 318, S.P. value 9.0], etc. can be mentioned.)

[0016] Moreover, although these ester may be used independently, in order to adjust them in the viscosity range according to various kinds of applications mentioned later Combination use of equipment may be carried out suitably, for example, it is organic complex type carboxylate of the above (3). When viscosity is high With the ester oil of aliphatic series polyhydric alcohol and a fatty acid, the viscosity in 40 degrees C is 100mm<sup>2</sup>/s. The following can be added and it can adjust to the viscosity range according to an application.

[0017] Moreover, it is good to add polymers to organic carboxylate oil, when viscosity is low, and to adjust viscosity. For a polymer, the viscosity in 40 degrees C is 1000mm<sup>2</sup>/s. The above thing is desirable. As such a polymer, it is shown by the following type with the polyester of poly alkyl methacrylate (an alkyl group is the thing of carbon numbers 1-9 in a straight chain part), polyalkylene glycols (for example, the copolymer which consists of a polypropylene glycol, and a polyethylene-glycol component and a polypropylene-glycol component, the copolymer which consists of a polypropylene-glycol component and a polytetramethylene glycol component), neopentyl glycol, and an aliphatic series dibasic acid. [0018]

[Formula 3]



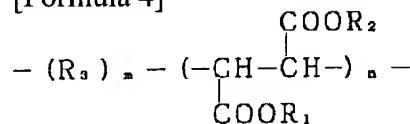
[0019] \*\* can be mentioned. Although the addition of a polymer is not especially limited if the ester oil which has desired viscosity and compatibility is obtained, it can usually be made into 1 % of the weight - 99% of the weight of the range.

[0020] A multiple-valued carboxylic acid as multiple-valued carboxylate Moreover, 1, 2, 3, 4-butane tetracarboxylic acid, Aliphatic series, such as cyclohexane-carboxylic-acid, 1, and 4-cyclohexane carboxylic acid, The monohydric alcohol in which it is an alicyclic multiple-valued carboxylic acid, and alcohol has the alkyl group of the shape of a straight chain or branching or general formula H-(AO) n-R (the inside A of a formula -- the alkylene group of carbon numbers 2-9 --) The thing of the mono-all object of a polyalkylene glycol in which R is shown by the straight chain part and the alkyl group of carbon numbers 1-9 and n are shown for the integer of 1-10 is mentioned. Moreover, the multiple-valued carboxylate which is made to carry out the esterification reaction of these polyhydric alcohol and alcohol, and is obtained Or the complex ester which is made to add and carry out the esterification reaction of the polyhydric alcohol, such as ethylene glycol and propylene glycol, to the above-mentioned multiple-valued carboxylic acid and alcohol further, and is obtained is mentioned.

[0021] Next, fumaric-acid ester oligomer is explained. Fumaric-acid ester oligomer is the gay polymer of fumaric-acid ester, or the copolymer of fumaric-acid ester and partial saturation aliphatic hydrocarbon, and is shown by the following type. The both ends in the following formula are polymerization initiator residue used on the occasion of a polymerization reaction, and are omitting the publication in a formula.

[0022]

[Formula 4]

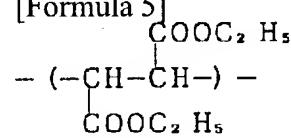


[0023] the inside of a formula, R1, and R2 -- the alkyl group of the shape of the straight chain of 1-9 carbon atoms, or branching -- Or they are a permutation and a non-permuted polyalkylene oxide radical in the alkyl group of the shape of a straight chain or branching. Even if the same, it may be different, and it is R3. The straight chain, branching, or the annular alkylene group of carbon numbers 2-12, the alkylene group permuted by the alkyl group of the shape of a straight chain and branching or a polyalkylene oxide radical, and m -- 0 or more and n -- one or more -- desirable -- the integer of 1-12 -- it is -- R3 It is less than [ of the whole / 50 mol % ].

Specifically, the ester oligomer of diethylfumarate, the ester oligomer of dibutylfumarate, etc. are mentioned.

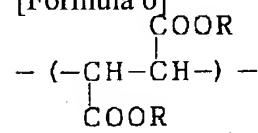
[0024] Moreover, the following structure expression [0025]

[Formula 5]



[0026] It is the 1-50-mol % and following general formula about the structural unit come out of and shown. [0027]

[Formula 6]

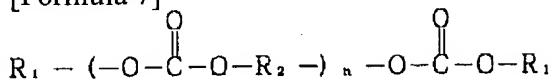


[0028] the structural unit shown by (the inside of a formula and R are the alkyl groups of the shape of the straight chain of 3-8 carbon atoms, or branching independently, respectively) -- 50 - 99-mol % -- the

included fumaric-acid alkyl ester copolymer can be mentioned.

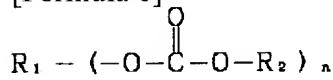
[0029] Next, as carbonates, it is a general formula. [0030]

[Formula 7]



[0031] They are the carbonates expressed with (R1 has the alkyl group of the shape of the straight chain of 2-10 carbon atoms, or branching among a formula, and R2 has 2-10 carbon atoms, and a nine or less carbon atom alkylene group or a cyclo alkylene group, and n are the integers of 1-4 in a straight chain part), or a general formula. [0032]

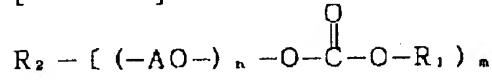
[Formula 8]



[0033] The carbonates expressed with (the alkyl group of the shape of the straight chain of 2-10 carbon atoms or branching and n of the polyhydric-alcohol residue in which R1 has 2-9 hydroxyl groups among a formula, and R2 are the integers of 2-6) can be used. The above-mentioned carbonates may manufacture dimethyl carbonate and alcohols by the ester exchange reaction under existence of a basic catalyst.

[0034] Moreover, a general formula [0035]

[Formula 9]



[0036] the inside of a formula, and R1 -- the alkyl group of the shape of the straight chain of 2-10 carbon atoms, or branching -- R2 The integer of 2-10 and n of the alkylene group of the shape of the straight chain of 2-10 carbon atoms or branching and m may be the integers of 2-100, and -CH<sub>2</sub>-CH<sub>2</sub>-O- is [ -AO- may have desirable -CH<sub>2</sub>-CH(CH<sub>3</sub>)-O-, and ] sufficient. The carbonates expressed can be used. Although these carbonates make carbonic acid and alkylene oxide react and it is obtained, a 2-3-mol thing is suitable for that amount of alkylene oxide addition. Moreover, an ethyleneoxide independent or a propylene oxide independent are sufficient as the addition gestalt of alkylene oxide, and a mixture is sufficient as it.

[0037] It sets to the ester oil with which a \*\*\*\* is mixed, and sodium and/or potassium levels are 0.1 ppm. It is as follows and it is desirable that it is what has the electrical resistivity more than 1x10<sup>14</sup>-ohmcm (25 degrees C). Although an acid catalyst, for example, phosphoric acid, generally carries out the bottom esterification reaction of existence of alcohols and the fatty acids and the polyol polyester mentioned above is obtained, according to such the method of preparation, that 5-50 ppm and whose moisture 0.1 - 0.5mg KOH/g and ash content (a part for a part for a part for a part for sodium and a potassium, iron, and titanium and silicon etc.) are generally 300-1000 ppm for the total acid number is obtained.

[0038] If the acid number is high, it is easy to produce problems, such as corrosion, in a metal part, and is not desirable as refrigerating machine oil. For this reason, the total acid number as refrigerating machine oil is 0.1mg KOH/g. It is 0.05mg KOH/g preferably the following. It is good to consider as the following. Moreover, in ester oil, although it was thought that the insulation of a lubricating oil changed with the impurity in the acid number or an oil, even if the acid number is high, the effect which it has on insulation is unexpectedly small, and no ash content in ester oil correlates it with insulation. Although the amount of [ a part for iron and titanium, ] silicon etc. does not affect the insulation in the ash content considered to mix the factor matter which lowers the volume resistivity of ester oil with the catalyst used at the inside of a raw material, or a synthetic process, the neutralizer further used at a purification process, if the total amount concentration for a part for sodium and a potassium in an oil exceeds 0.1 ppm, insulation will fall extremely.

[0039] It is desirable to face to refine a polyol ester, fumaric-acid ester oligomer, a carbonate, and hydroxy pivalate ester, and to adopt the purification means which does not contain the component given to insulation, and when especially the amount of sodium adopts the approach of avoiding use of the compound which uses sodium as a configuration element by purification since removal is difficult, the ester which shows high insulation at few purification processes can be obtained. As an approach of avoiding a part for sodium, it is useful to use a potassium hydroxide, a calcium hydroxide, etc. for neutralization of the free fatty acid after an esterification reaction, for example. Moreover, in order to raise refrigerant stability, it is peroxide \*\*1meq./Kg. Following and aldehyde \*\* 1mg KOH/g It is good to be hereafter referred to as the bromine-number characteristic of 10mg / 100g or less.

[0040] It is good for contact processing to perform purification of the ester mixed with silica gel, an activated alumina, activated carbon, a zeolite, etc. The contact conditions in this case are good to set suitably according to various situations, and, as for temperature, it is desirable to carry out below 100 degrees C. As other ester purification approaches, although cost becomes high, it is good also by the approach by ion exchange resin or the inorganic ion exchanger (product made from the Toagosei chemistry).

[0041] The mixed rate of the ester mixed to hydroxy pivalate ester is preferably good to consider as 30 % of the weight - 50 % of the weight still more preferably 20 % of the weight to 50% of the weight 20 % of the weight to 60% of the weight, and since it becomes difficult for a volume resistivity to fall if 60 % of the weight is exceeded, for printing-proof nature to fall if fewer than 20 % of the weight, and to secure the viscosity clade of VG68, it is not desirable.

[0042] Next, generally, since the electrical resistivity of refrigerating machine oil is reduced, even if this kind of additive makes high electrical resistivity of the ester oil mentioned above and adds an additive, it is good [ additive ], although it is good for the refrigerating machine oil of this invention to add an antioxidant, corrosion inhibitor, an antiwear agent, a defoaming agent, a metal deactivator, a rust-proofer, etc. to make it become desired electrical resistivity.

[0043] As an anti-oxidant, for example A JI (alkylphenyl) amine (an alkyl group is carbon numbers 4-20), A phenyl-alpha-naphthylamine, an alkyl diphenylamine (an alkyl group is carbon numbers 4-20), An N-nitroso diphenylamine, phenothiazin, N,N'-dinaphthyl-p-phenylenediamine, An acridine, N-methyl phenothiazin, N-ethyl phenothiazin, Amine system antioxidants, such as a dipyridyl amine, diphenylamine, phenol amine, 2, and 6-G t-butyl-alpha-dimethylamino PARAKU resol, 2.6-G t-butyl PARAKUREZO-RU, 4,4'-methylenebis (2.6-G t-butylphenol), 2.6-G t-butyl-4-N and N-dimethylamino methyl phenol, A phenolic antioxidant and iron octoate, such as 2.6-G t-butylphenol, Organic iron salt, such as a ferrocene and iron naphthoate, cerium naphthoate, It is good to use FOSU fights, such as organometallic compound system anti-oxidants, such as organic JIRIKONIUMU salts, such as organic cerium salts, such as cerium toluate, and JIRIKONIUMU octoate, and also a TORIJI-t-buthylphenyl FOSU fight, and a trioctyl FOSU fight. Moreover, although the above-mentioned antioxidant may be used independently, as the synergistic effect is done so, it can also use it by using two or more sorts, combining. The operating rate of an antioxidant is good to use 0.01 - 2 % of the weight preferably 0.001 to 5% of the weight to base oil.

[0044] As corrosion inhibitor, there are isostearate, n-octadecyl ammonium stearate, DEYUOMIN T and DEORETO, naphthenic-acid lead, sorbitan olate, pen TAERI slit olate, oleyl ZARUKOSHIN, an alkyl succinic acid, alkenyl succinic acids, these derivatives, etc., and the operating rate is good to use it 0.01 to 0.5% of the weight preferably 0.001 to 1.0% of the weight to ester base oil.